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Spin frustration and concealed asymmetry: structure and magnetic spectrum of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ †

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The oxo-centred trinuclear complex $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ and its fully deuteriated analogue have been synthesized. X-Ray crystallography at $T = 233$ K shows that the complex has threefold symmetry, space group $P6_3/m$. Incoherent inelastic neutron scattering spectra at $T = 1.5$ K however show the presence of two inequivalent sets of molecules, one a static "isosceles" coupled system, with two J values for the three metal–metal interactions, the other a dynamic system, with rapid pseudorotation between equivalent isosceles geometries. Combining infrared and neutron scattering data, the distortion of the cluster has been estimated.

Introduction

An assembly of spins located on an assembly of atoms may not be able to adopt a coupling scheme with symmetry compatible with the atomic framework. The simplest case is that of three half-integral spins located at the corners of an equilateral triangle, which cannot couple antiferromagnetically with threefold symmetry. In an extended lattice the resulting spin frustration leads to canted spin structures.[1]

In an isolated molecule it has been proposed[2] that this spin frustration will lead to a geometrical distortion. Trinuclear oxo-centred, carboxylate bridged complexes of general formula $[M^{III}{}_3O(O_2CR)_6L_3]^+$ can be used to test this theory. In crystallographic studies of such complexes it has usually been found that the complex cation does not occupy a site with threefold crystallographic symmetry.[3] However there are a few exceptions,[4,5] and one which we have studied is the chromium(III) complex[6] $[Cr_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}0.5py$. Although the room temperature crystal structure has the space group $P6_3/m$, with the trimer complexes stacked on parallel threefold axes, low temperature inelastic incoherent neutron scattering (IINS) spectra imply a breaking of symmetry. The molecules are distorted to a very small extent but the distortions are concealed either by rotational disorder in the crystal structure or by pseudorotation at rates greater than the timescale of the techniques, in the glassy and solution states.

We now find the complex $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ to be isostructural with the chromium complex, and low-temperature IINS spectra again indicate a reduction in molecular symmetry. However, in this case the whole of the allowed spectrum is well resolved and has revealed a situation not previously seen: half of the molecules adopt an "isosceles" form with one iron atom magnetically distinct from the other two; the other half adopt what we call a "scalene" form. This can be modelled with three different Fe–Fe coupling constants; the molecules may either be static or dynamic undergoing pseudorotation with no net preference for distortion in any one direction.

Results and discussion

The structure of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ is shown in Fig. 1. At 233 K the unit cell contains two equivalent molecules of D_3 symmetry on parallel threefold axes. The molecules are stacked on the axes with a molecule of unco-ordinated pyridine between them, perpendicular to the axis and rotationally disordered. The perchlorate counter ions also occupy threefold sites and are disordered. The iron–central oxygen bond lengths are 1.915 ± 0.001 Å. The metal ions have distorted octahedral geometry, metal–carboxylate bond distances 2.014 ± 0.003, metal–nitrogen 2.206 ± 0.006 Å. By imposed symmetry the central oxygen is in the same plane as the three iron atoms. The nitrogen and γ-carbon atoms of the pyridines lie on the plane, and the co-ordinated pyridines are perpendicular to the plane. The benzoate bridging groups have carbon–oxygen distances of 1.270 ± 0.006 and 1.268 ± 0.006 Å.

The structure is directly comparable to that of the recently published nitrate complex $[Fe_3O(O_2CPh)_6(py)_3]NO_3{\cdot}CH_2Cl_2$[7] which shows a similar packing arrangement with the molecules stacked on threefold axes interleaved by disordered solvate molecules and the counter ions again on the other threefold axes.

The IINS spectrum (Fig. 2) shows eight well defined transitions identifiable as magnetic from the Q dependence, at energy transfers of 2.27, 3.4, 5.0, 8.1, 9.3, 10.6, 11.3, 13.1 meV.

In order to model the coupling we have assumed a spin-only model; the contribution of other effects such as spin–orbit coupling to systems of this type with no orbital degeneracy can be assumed to be negligible.[8] As discussed elsewhere,[9] the spin-only model leads to a manifold of states with total spin $S = \frac{1}{2}, \frac{3}{2}$, *etc.* Previous oxo-bridged systems studied are all antiferromagnetic and require more than one coupling constant per metal triangle. Any distortion leading to inequality of the coupling constants splits the S levels, and the selection rules for IINS allow four transitions from the ground state, one within the $S = \frac{1}{2}$ manifold, three from $S = \frac{1}{2}$ to $\frac{3}{2}$. For the isosceles case, *i.e.* two J values, the ground state is $|S, S_{ab}\rangle = |\frac{1}{2}, 2\rangle$ or $|\frac{1}{2}, 3\rangle$ for $-J$ greater or less than $-J_{ab}$, where $J = J_{bc} = J_{ca}$, and c labels the unique atom. For the scalene case, *i.e.* three J values, Thompson and co-workers[10] showed that energies and transition probabilities can be interpolated from the limiting isosceles cases, provided that the differences between J values are not too great. In such cases the quantum number S_{ab} is not defined, but S is still a good quantum number, and there are four transitions

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† Electronic supplementary information (ESI) available: IR frequencies and assignments for $[M_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$. See http://www.rsc.org/suppdata/dt/b0/b008121n/

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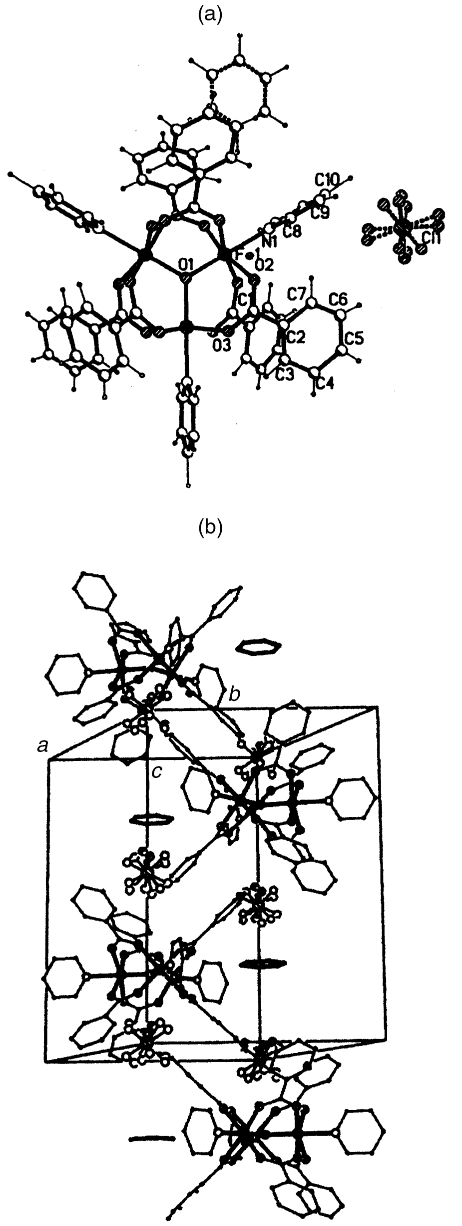

Fig. 1 Crystal structure of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$, viewed along the *c* axis (above) and showing the lattice packing in isometric projection (below).

of appreciable intensity corresponding to the four allowed transitions of the isosceles case.[9]

Our spectrum, with eight bands, supports a structure with two sets of molecules, in equal numbers, differently distorted. The basis of the fit is that, on each of the three models, the energy difference between the highest and second-highest transition is equal to the observed energy of the lowest transition. This leads directly to assignment of the four bands to each of two sets, A and B, as labelled in Fig. 2.

The peaks assigned as A are fitted well by an isosceles model with ground state $|\tfrac{1}{2}, 2\rangle$, $J = -3.54 \pm 0.03$, $J_{ab} = -3.18 \pm 0.01$ meV. Among the four peaks assigned as B however, 2, 3 and 4 are almost equidistant, with separations in good agreement with that of band 1. This is consistent with the "scalene" model in its extreme limit, in which the three Fe–Fe coupling constants are equally separated, $\langle J\rangle$ and $\langle J\rangle \pm 9$ D.§ On this model the energies of the allowed transitions are $9D$, $-3\langle J\rangle - 9D$, $-3\langle J\rangle$, $-3\langle J\rangle + 9D$, giving $\langle J\rangle = -2.65 \pm 0.03$, $D = 0.36 \pm 0.01$ meV, where D is the distortion parameter and is a measure of the magnitude of the difference between non-equivalent sites. The calculated energies listed in Table 1 are based on least-squares fits to the observed energies, weighted by the calculated relative intensities. The calculated and observed spectra are compared in Fig. 2.

Table 1 Calculated and observed IINS spectra for $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$

Band	Energy (obs.)/meV	Assignment^a		Energy (calc.)/meV
i	2.3 ± 0.1	A1	$|\tfrac{1}{2}, 3\rangle$	2.3
ii	3.4 ± 0.2	B1	$|\tfrac{1}{2}\rangle$	3.2
iii	4.9 ± 0.1	B2	$|\tfrac{3}{2}\rangle$	4.8
iv	8.2 ± 0.1	B3	$|\tfrac{3}{2}\rangle$	8.0
v	9.35 ± 0.15	A2	$|\tfrac{3}{2}, 1\rangle$	9.3
vi	10.65 ± 0.1	A3	$|\tfrac{3}{2}, 2\rangle$	10.8
vii	11.35 ± 0.1	B4	$|\tfrac{3}{2}\rangle$	11.2
viii	13.15 ± 0.1	A4	$|\tfrac{3}{2}, 3\rangle$	13.1

[a] Ground state for bands A, $|S, S_{ab}\rangle = |\tfrac{1}{2}, 2\rangle$; for bands B, $|S\rangle = |\tfrac{1}{2}\rangle$.

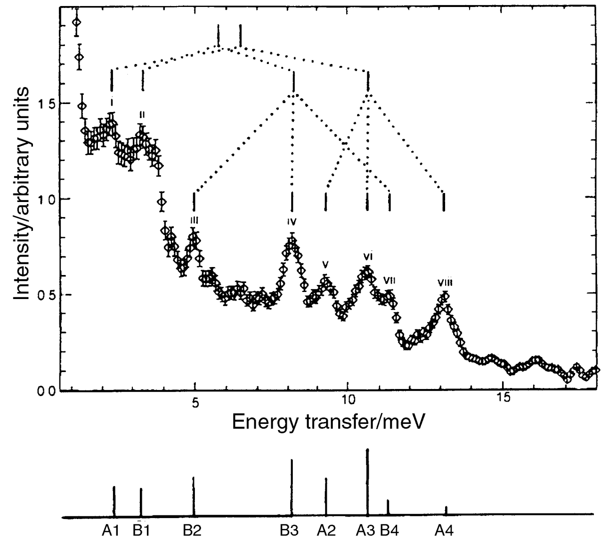

Fig. 2 IINS of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$; $T = 1.5$ K; incident neutron energy 25 meV. Measured on a MARI spectrometer at ISIS-RAL.

Intermolecular coupling

An intermolecular coupling contribution has been considered for the complex $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl{\cdot}6H_2O$ but was convincingly ruled out.[11] In the present case the possibility should be considered more seriously since π overlap between the interleaved phenyl groups could provide a plausible exchange pathway. Moreover an intermolecular model also predicts just 8 observable transitions, though as we will now show the quantitative fit proves to be unconvincing. Using the spin-only model as before we derive expression (1) for the energy of a pair of

$$\begin{aligned} E = -J[&S_1(S_1+1) - S_{1a}(S_{1a}+1) - S_{1b}(S_{1b}+1) - \\ &S_{1c}(S_{1c}+1) + S_2(S_2+1) - S_{2a}(S_{2a}+1) - \\ &S_{2b}(S_{2b}+1) - S_{2c}(S_{2c}+1)] - \\ &J_{12}[S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)] \qquad (1) \end{aligned}$$

clusters, with a single intramolecular coupling constant J and intermolecular coupling constant J_{12}, where subscripts 1 and 2 label the two clusters, a, b, c the atoms in a cluster, and $S_{12} = S_1 + S_2$. There are two possible ground states, and ten allowed transitions from either of them, but we expect J_{12} to be very small compared to J, so the lowest energy transition would be too small to be observed. Also two of the other predicted transitions have the same energy, leaving a total of eight

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§ Ref. 9(*b*), eqns. 9–11; ref. 9(*c*), eqns. 8–10; with $\theta = 30°$.

Table 2 Summary of data used to calculate distortion of the metal triangle in complexes $[M_3O(O_2CPh)_6(py)_3]$

M	ν_{asym}/cm^{-1}	Band width/cm^{-1}	ΔE/cm^{-1}	x/Å
Cr	650	16.7	1.1	0.003
Fe	622	12.5	18.2	0.009

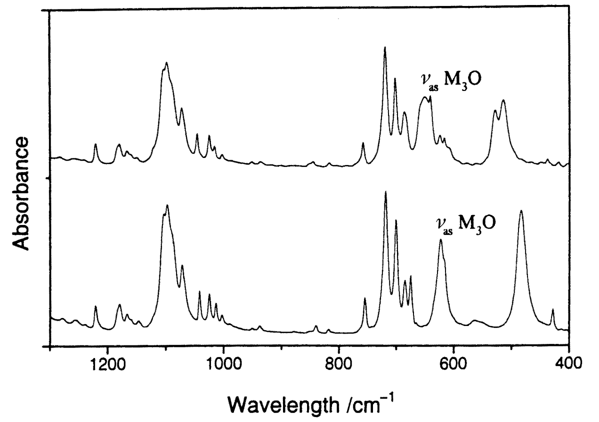

Fig. 3 IR spectra of $[Cr_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ (above) and $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$ (below); $T = 298$ K; central oxygen asymmetric stretching mode, ν_{asym} M_3O marked.

observable bands. However with this model the fit of band energies to the observed spectrum is poor with much larger discrepancies than those indicated in Table 1. The coupling constants obtained from this fit are also unrealistic, $J = -1.32$, $J_{12} = -0.56$ meV.

Estimating the magnetic Jahn–Teller distortion

Accepting that the trinuclear cluster is distorted at low temperature, this can be explained as symmetry breaking which avoids the degeneracy of an equilateral exchange coupled system.[6,9] There is strong evidence that the central oxygen provides the main superexchange pathway,[12] so the most significant distortion would be movement of the central oxygen away from the centre of the triangle of metal atoms. We can use this to obtain an estimate of this movement of the central oxygen if we equate the elastic strain energy required for this to the energy gained by splitting the electronic ground state, eqn. (2) where ΔE is

$$\frac{1}{2}\Delta E = \frac{1}{2}kx^2 = \frac{1}{2}(4\pi^2\nu_{asym}{}^2mx^2) \qquad (2)$$

the energy of the lowest-energy IINS transition, k the force constant of the asymmetric O–M_3 stretch, m the mass of the oxygen atom and x the displacement from the centre of the triangle. This assumes that the motion involved in ν_{asym} is predominantly that of the central oxygen: isotopic replacement studies on related molecules show that this is a fairly good approximation.[13] In this work we find $\nu_{asym}(M_3O)$ at 650 cm^{-1} for the chromium complex and 622 cm^{-1} for the iron complex (Fig. 3), thus we can estimate the distortions in the two complexes, as shown in Table 2. In principle such distortion splits $\nu_{asym}(M_3O)$ and in some oxo-centred copper(II) complexes the analogous splitting has been observed.[13]

It has previously been shown that small structural distortions can sometimes lead to a lifting of the degeneracy of vibrations even when the distortion cannot be seen in the crystal structure.[14] However in the present case the bands are too broad to show splittings of the expected magnitude. Using the methods of reference 13(*b*) we derive eqn. (3) where $\langle\nu\rangle$ is the mean frequency, $\Delta\nu$ the difference in frequency of the components of $\nu_{asym}(M_3O)$, $\langle d\rangle$ the mean Fe–Fe distance, and x the displacement of the central oxygen atom from the centre of the triangle. The calculated splitting is 1.4 cm^{-1} for the iron complex compared with a band width of 12.5 cm^{-1} measured at room temperature. The same calculation for the chromium complex gives a splitting of less than 0.5 cm^{-1}.

$$\frac{\Delta\nu}{\langle\nu\rangle} = \left(\frac{1}{\sqrt{3}}\right)\frac{\chi}{\langle d\rangle} \qquad (3)$$

It is important to note that the infrared data used in the above estimations were collected at room temperature; cooling over a range of 300 K is likely to produce shifts in band position as well as a decrease in band widths. Shifts in $\nu_{asym}(M_3O)$ of up to 30 cm^{-1} result in a change in the estimate of x of ±0.0004 Å. It is likely that any splitting, due to sharpening of the bands on cooling, would be hidden by overlap.

Conclusion

The presence of eight bands in the IINS spectrum provides compelling evidence that, at least at low temperature, the molecules have less than threefold symmetry, supporting the theory that spin frustration will drive a distortion of the molecular symmetry. The presence of inequivalent molecules at low temperature suggests that the complex either undergoes a phase transition on cooling or that there is a dynamic disorder in the structure which, while masked at higher temperatures, is "frozen-out" at low temperature.

Superexchange has now been studied in a large number of oxo-centred trinuclear complexes, and in every case in which the coupling is antiferromagnetic more than one coupling constant is required. This is well known, but especially significant are the complexes which show threefold crystallographic symmetry, at room temperature. In the three cases which have been adequately studied the pattern of coupling constants at low temperature is what we have defined here to be scalene in the extreme limit, *i.e.* the three J values are equally separated. The complexes are $[Fe_3O(SO_4)_6(H_2O)_3]$,[4,9c,15] $[Fe_3O(O_2CCMe_3)_6(MeOH)_3]Cl$,[5,9c] and the present complex $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$. As Thompson and co-workers pointed out,[10] such a scheme is equally compatible with a dynamic model, in which the triangular cluster undergoes pseudorotation between isosceles conformations which are geometrically identical but rotated about the centre. It is interesting that the average J value is less than in the stationary, isosceles complex, -2.65 meV compared with $(2 \times 3.54 + 3.18)/3 = -3.42$ meV, suggesting a larger cavity a likely expectation for a freely rotating complex. A lower limit on the timescale of the experiment can be calculated from the lowest energy peak observed in the IINS spectrum; this gives a figure of 5.5×10^{-11} Hz as the lower limit and we assume pseudorotation to be occurring faster than this.

Experimental

Synthesis

CAUTION: perchlorate salts were assumed to be explosive and handled with great care, avoiding heat, friction and percussion.

$[Fe^{III}{}_3O(O_2CPh)_6(H_2O)_3]ClO_4$, 1. A solution of iron(III) chloride hexahydrate, $FeCl_3{\cdot}6H_2O$ (13.5 g, 0.05 mol), in water (50 cm^3) was added slowly to a solution of $PhCO_2Na$ (25 g, 0.17 mol) in water (300 cm^3). The flesh-coloured precipitate of iron benzoate formed was washed with water and dried at 40 °C. This material was first reported[16] as $[Fe_3(OH)_2(O_2CPh)_6][O_2CPh]$. A 2.0 g portion was mixed with 96% ethanol (35 cm^3) to give a milky orange suspension. On slow addition of 20% perchloric acid (6.0 g, 0.06 mol) the solution immediately cleared to give a deep orange solution, with only a small amount of solid. This solution was warmed gently on a steam bath for 10 minutes and then filtered hot. Boiling water (35 cm^3) was added to the still warm filtrate and an orange solid formed immediately. The solid was left to cool, filtered off in air, and washed with 1 : 1 water–acetone (25 cm^3). The resulting orange powder was dried in a desiccator over concentrated sulfuric acid (Found: C, 47.4; H, 3.39; Cl, 3.34. $C_{42}H_{36}ClFe_3O_{20}$ requires C, 47.9; H, 3.86; Cl, 3.24%). The powder obtained from this preparation is of good quality. A more crystalline product can be obtained if the water used is hot, but not boiling. This results in a slower precipitation but also gives a slightly lower yield.

$[Fe^{III}_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$, 2. *Method 1.* A portion of complex **1** (3.0 g, 2.8 × 10^{-3} mol) was stirred into pyridine (200 cm^3), giving a dirty brown suspension. This was heated on a steam bath for 2 hours until all the solid had dissolved leaving a clear red-brown solution. The solution was filtered and left to recrystallise slowly. On filtration a tan powder was obtained. (Found: C, 56.0; H, 3.62; Cl, 2.86, N, 4.11. $C_{62}H_{50}ClFe_3N_4O_{17}$ requires C, 56.2; H, 3.80; Cl, 2.68; N, 4.23%).

Method 2. A more direct method was based on the preparation of the analogous chromium(III) compound.[17] Benzoic acid (6.1 g, 0.05 mol) was dissolved in pyridine (50 cm^3). Iron(III) perchlorate hydrate, $Fe(ClO_4)_3{\cdot}xH_2O$ (7.2 g), was added quickly with swirling. It did not dissolve completely but the mixture immediately turned a murky orange-red-brown and became warm. After refluxing for 1 h 40 min the dark red-brown suspension was left to cool. The cooled solution was filtered and washed with a small quantity of diethyl ether. Sometimes this method of preparation produced an impure product, contaminated with starting material. Washing with water removed the contaminant and the sample can then be recrystallised from pyridine. Otherwise, the solid thus obtained was a powder, varying from a dark tan colour to a pale sandy yellow-brown. The colour seems to be related to particle size rather than to the purity, as all powders obtained after washing gave identical IR spectra and similar analyses. The product also always appears to have one pyridine molecule of crystallisation (Found: C, 56.2; H, 3.51; Cl, 3.17; N, 4.14%). A microcrystalline sample was obtained by very slow recrystallisation from pyridine in a warm oven (at approx. 48–50 °C). The perdeuterio analogue was prepared using this direct method, using perdeuteriopyridine and perdeuteriobenzoic acid (99.5% D; Aldrich) (Found: C, 53.0; N, 3.97; Cl, 2.66. $C_{62}D_{50}ClFe_3N_4O_{17}$, assuming 99% deuteriation, requires C, 54.1; N, 4.07; Cl, 2.58%). The compounds were stored in dry air.

Structure determination and refinement

Data were measured on a Rigaku AFC7R diffractometer with Mo-Kα radiation; a reddish brown crystal was cooled to 233 K using an Oxford Cryostream low-temperature system. Details of the data collection and structure refinement are summarised in Table 3. The structure was solved and refined using the SHELXTL software package.[18] The perchlorate anion lies on the special position at {0,0,0} and found to be heavily disordered. The pyridine of solvation is centred at {2/3, 1/3, 1/4} and is rotational disordered; it was refined with each atom $\frac{5}{6}$ CH and $\frac{1}{6}$ N. H atoms were placed in calculated positions. All non-H atoms were assigned anisotropic thermal parameters except the oxygens of the perchlorate anion.

CCDC reference number 152797.

See http://www.rsc.org/suppdata/dt/b0/b008121n/ for crystallographic data in CIF or other electronic format.

IINS

IINS spectra of the fully deuteriated material were measured on the MARI spectrometer at ISIS-RAL, using incident neutrons of energy 25 meV. Data reduction was carried out using the standard in-house program. All reported spectral features were confirmed to be magnetic on the basis of the momentum transfer dependence of the intensity.

Table 3 Crystal data and structure refinement for $[Fe_3O(O_2CPh)_6(py)_3]ClO_4{\cdot}py$

Empirical formula	$C_{62}H_{50}ClFe_3N_4O_{17}$
Formula weight	1326.06
T/K	233(2)
λ/Å	0.71069
Crystal system	Hexagonal
Space group	$P6_3/m$
a/Å	13.541(3)
b/Å	13.541(3)
c/Å	19.136(5)
V/Å^3	3038.7(12)
Z	2
μ/mm^{-1}	0.824
Reflections collected	1687
Independent reflections	1477 [R_{int} = 0.0416]
Absorption correction	None
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1477/3/149
$wR2$, $R1$ (all data)	0.1207, 0.1241
[$I > 2\sigma(I)$]	0.0993, 0.0429

Infrared spectroscopy

Spectra were recorded from KBr discs on a Unicam Mattson 5000 FT-IR spectrometer with a resolution of 2 cm^{-1} for 128 scans over the range 4000–400 cm^{-1}. Assignments were made based on comparison of the perdeuterio complex with the undeuteriated analogue and by comparison with literature spectra.[19] The infrared spectra and assignments of the iron and chromium complexes are available as supplementary data.†

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References

1 A. P. Ramirez, *Annu. Rev. Mater. Sci.*, 1994, **24**, 453; A. Harrison, *J. Phys. C: Solid State Phys.*, 1987, **20**, 6287; A. S. Wills and A. Harrison, *J. Chem. Soc., Faraday Trans.*, 1996, 2161; J. L. Manson, E. Ressouche and J. S. Miller, *Inorg. Chem.*, 2000, **39**, 1135.

2 T. Murao, *Phys. Lett.*, 1974, **49A**, 33.

3 R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195; D. Weatherburn, personal communication.

4 R. E. Watson and A. J. Freeman, *Acta Crystallogr.*, 1961, **14**, 27.

5 A. B. Blake and L. R. Frazer, *J. Chem. Soc., Dalton Trans.*, 1975, 193.

6 R. D. Cannon, U. A. Jayasooriya, F. E. Sowrey, C. Tilford, A. Little, J. P. Bourke, R. D. Rogers, J. B. Vincent and G. J. Kearley, *Inorg. Chem.*, 1998, **37**, 5675.

7 A. M. Bond, R. J. H. Clark, D. G. Humphrey, P. Panayiotopoulos, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 1845.

8 A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, 45; V. A. Gaponenko, M. V. Eremin and Yu. V. Yablokov, *Sov. Phys. Solid State*, 1973, **15**, 909.

9 (*a*) U. A. Jayasooriya, R. D. Cannon, R. P. White and G. J. Kearley, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 930; (*b*) U. A. Jayasooriya, R. D. Cannon, R. P. White, J. A. Stride, R. Grinter and G. J. Kearley, *J. Chem. Phys.*, 1993, **98**, 9303; (*c*) R. D. Cannon, U. A. Jayasooriya, R. Wu, S. K. arapKoske, J. A. Stride, O. F. Nielsen, R. P. White, G. J. Kearley and D. Summerfield, *J. Am. Chem. Soc.*, 1994, **116**, 11869. Errata: in ref. 9(*c*), eqns. 10b, 10c and 10d, the signs preceding the cos 3θ term should be −, +, − respectively.

10 D. M. Jones, J. R. Sams and R. C. Thompson, *J. Chem. Phys.*, 1984, **81**, 440.

11 B. S. Tsukerblat, M. I. Belinskii and B. Ya. Kuyavskaya, *Inorg. Chem.*, 1983, **22**, 995.

12 A. B. Blake, A. Yavari, W. E. Hatfield and C. N. Sethulekshmi, *J. Chem. Soc., Dalton Trans.*, 1985, 2509; A. B. Edwards, J. M.

Charnock, C. D. Garner and A. B. Blake, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2515.

13 (*a*) L. Meesuk, U. A. Jayasooriya and R. D. Cannon, *Spectrochim. Acta*, *Part A*, 1987, **43**, 687; (*b*) R. Wu, U. A. Jayasooriya and R. D. Cannon, *Spectrochim. Acta*, *Part A*, 2000, **56**, 575.

14 C. E. Anson, S. K. arapKoske, U. A. Jayasooriya and R. D. Cannon, *Spectrochim. Acta*, *Part A*, 1992, **48**, 151; S. J. Eames and R. D. Cannon, *Spectrochim. Acta*, *Part A*, 1996, **52**, 1101.

15 A. Furrer and H. U. Güdel, *Helv. Phys. Acta*, 1977, **50**, 439.

16 R. F. Weinland and A. Herz, *Ber. Detsch. Chem. Ges.*, 1912, **45**, 2662.

17 M. M. Glass, K. Belmore and J. Vincent, *Polyhedron*, 1993, **12**, 133.

18 SHELXTL, Version 5, Siemens Industrial Automation, Inc., Analytical Instrumentation Business Unit, Madison, WI, 1995.

19 C. H. Kline and J. Turkevich, *J. Chem. Phys.*, 1944, **7**, 300; K. B. Wiberg, V. A. Walters, K. N. Wong and S. D. Colson, *J. Chem. Phys.*, 1984, **88**, 6067; G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives. Vol. 1*, Academic Press, New York, 1974; A. M. Harton, K. Nagi, M. M. Glass, P. C. Junk, J. L. Atwood and J. B. Vincent, *Inorg. Chim. Acta*, 1994, **217**, 171; L. Meesuk, U. A. Jayasooriya and R. D. Cannon, *J. Am. Chem. Soc.*, 1987 **109**, 2009; R. P. White, Ph.D. Thesis, University of East Anglia, 1988; M. K. Johnson, D. B. Powell and R. D. Cannon, *Spectrochim. Acta*, *Part A*, 1987, **37**, 995.